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ANALYTICAL VARIABILITY OF FIVE WASTEWATER PARAMETERS - PETROLEUM REFINING INDUSTRY

Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma

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Samples were divided among 12 laboratories to be analyzed for chemical oxygen demand, suspended solids, ammonia nitrogen, phenolics, and oil and grease. The Robert S. Kerr Environmental Research Laboratory analyzed six sample sets to determine intralaboratory deviation (repeatability), while the other participating laboratories analyzed single samples to provide data for interlaboratory deviation (reproducibility) determinations. Study results are expressed in terms of averages, standard deviation, and spike recoveries for intralaboratory, interlaboratory, and combined evaluations.

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ANALYTICAL VARIABILITY OF FIVE WASTEWATER PARAMETERS--PETROLEUM REFINING INDUSTRY

by

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ABSTRACT

Information is presented on a "Round Robin" laboratory analysis exercise conducted by Environmental Protection Agency laboratories with comparative industrial and state agency laboratories. The initial sample analyzed was obtained from a petroleum refinery activated sludge plant's final clarifier effluent and represented a low contaminant level wastewater. The second sample was taken from the discharge of an American Petroleum Institute separator at a refinery and was characteristic of a high contaminant level wastewater containing sulfide concentrations which could cause analytical interferrence problems.

Samples were divided among 13 laboratories to be analyzed for chemical oxygen demand, suspended solids, ammonia nitrogen, phenolics, and oil and grease. The Robert S. Kerr Environmental Research Laboratory analyzed six sample sets to determine intralaboratory deviation (repeatability), while the other participating laboratories analyzed single samples to provide data for interlaboratory deviation (reproducibility) determinations. Study results are expressed in terms of averages, standard deviation, and spike recoveries for intralaboratory, interlaboratory, and combined evaluations.

A summary of the instruction seminar which was provided to the participants between the low and high level sample runs to discuss analytical problems and techniques used for the five parameters is presented.

This report was submitted by the Robert S. Kerr Environmental Research Laboratory under the sponsorship of the Environmental Protection Agency. Work was completed as of June, 1974.

CONTENTS

Sections		Page
I	Conclusions	1
II	Recommendations	3
III	Introduction	4
IV	Participant Selection	5
V	Study Objective	9
VI	Study Conditions	11
VII	Sampling Procedures	13
	Sample Sets	14
	Location of Sample Points	17
	Sample Delivery	17
VIII	Participant Seminar	18
IX	Statistical Evaluation	20
	Preliminary Data Checking	20
	Outlier Rejections	20
	Data Presentation	21
	Data Analyses	21
X	References	35
XI	Appendices	36

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FIGURES

No.		Page
1	Project Organisational Structure	6
2	Equipment Used to Obtain Representative Sample	14
3	Sampling Pump Installation	15
4	Composite Sampling Container	15
5	Top View of Composite Sampling Container	16
6	Sample Sets for Cooperative Laboratories	16
7	Chemical Oxygen Demand Set-Up	39
8	Phenolics Set-Up	39
9	Oil and Grease (Hexane Extraction) Set-Up	40
10	Ammonia Nitrogen Set-Up	40
11	Suspended Solids Set-Up	41

TABLES

No.		Page
1	Crude Capacity of Participants	7
2	Sample Volumes and Preservatives	17
3	TOC Analysis on Replicate Samples	19
4	COD Analytical Method Evaluation - Phase I	33
5	Suspended Solids Analytical Methods Evaluation - Phase I	34
6	Ammonia Analytical Method Evaluation - Phase I	35
7	Phenolics Analytical Method Evaluation - Phase I	36
8	Oil and Grease Method Evaluation - Phase I	37
9	COD Analytical Method Evaluation - Phase II	38
10	Suspended Solids Analytical Method Evaluation - Phase II	39
11	Ammonia Analytical Method Evaluation - Phase II	40
12	Phenolics Analytical Method Evaluation - Phase II	41
13	Oil and Grease Method Evaluation - Phase II	42
14	Statistical Comparison of Laboratory 01 with the Other Laboratories (at the 95% confidence level)	53
15	Statistical Comparison of the Hexane and Freon Methods for the Analysis of Oil and Grease (at the 95% confidence level)	54

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SECTION 1

CONCLUSIONS

1. The chemical oxygen demand (COD) test had a repeatability (single lab) expressed in terms of standard deviation of 8.5 milligrams per liter (mg/l) for petroleum refinery wastewater which had a COD average of 164 mg/l. Reproducibility (overall laboratories) for this same refinery wastewater exhibited a standard deviation of 15.0 mg/l.

2. Suspended solids with an average concentration of 10 mg/l had a standard deviation for repeatability of 1.8 mg/l and a standard deviation for reproducibility of 5.2 mg/l.

3. Results obtained for the ammonia test with an average concentration of 7.5 mg/l exhibited a repeatability standard deviation of 0.1 mg/l and a reproducibility standard deviation of 0.9 mg/l.

4. The repeatability standard deviation for phenolics was 0.2 mg/l for a sample containing 5.4 mg/l; the standard deviation for reproducibility of phenolics was 0.8 mg/l.

5. Oil and grease standard deviation for repeatability was 2.5 mg/l and reproducibility was 2.9 mg/l for a sample containing approximately 11 mg/l.

6. A t-test shows there to be no significant difference between the quantitative results of the hexane and freon procedures.

7. The variance of the analysis for oil and grease is less for the freon method than the hexane method.

8. Recovery of ammonia and COD spikes was greater than 95 percent after instruction seminar.

9. A comparison of results between Phases I and II indicate the instruction seminar, which was held to achieve uniformity of analytical procedures accomplished:

a. A significant reduction in arithmetic and extreme outlier value errors;
b. Enhancement of uniformity of laboratory technique;
c. Minimizing the COD mean values between intralaboratory and interlaboratory results;
d. Improved spike recovery for COD and ammonia;
e. The standard deviations for COD, ammonia, and phenolics were decreased.

10. Environmental Protection Agency (EPA) methodology for the parameters studied appeared applicable for this petroleum refinery wastewater when the analysts were properly instructed.

SECTION II

RECOMMENDATIONS

1. Similar studies should be conducted with other industrial discharges to evaluate variances for EPA procedures.

2. Instruction seminars need to be developed by EPA to properly instruct analysts, whose results will be used by EPA for self-monitoring of permit conditions and acquisition of data on demonstration grants.

3. Repeatability and reproducibility values should be established for each EPA procedure on various industrial wastewaters.

4. An EPA Laboratory Service should be established to continue a cross-match of methodology with wastewater discharge samples peculiar to a specific industry. This established laboratory should be able to accept a testing program semi-annually with participating industrial and regulatory laboratories.

5. Phase I of this study should be repeated to determine the effect of the training seminar on the low level parameters as opposed to the high level parameters of Phase II.

SECTION III

INTRODUCTION

Enactment of the Federal Water Pollution Control Act Amendments of 1972 provided this Nation with the legislation needed to clean up the domestic waters. This law specified two goals for reducing and eliminating water pollution: first, to provide water clean enough for swimming and other recreational purposes by July 1, 1983, and second, to eliminate pollutant discharges by July 1, 1985.

Within the framework of this legislation, industry discharging wastes must obtain a discharge permit issued under the regulation of EPA. The permit contains a description of the effluent limitations for the pollutants of concern. Enforcement of the issued permit is administered by EPA, either through monitoring stations or by site visits when samples of water discharges may be obtained and analyzed for permit compliance. The permit holder is required to provide analytical data on water discharges to EPA on a routine basis. If a permit holder is in violation of the permit conditions, court action may be pursued.

Since many states have legally provided a documented self-reporting system of effluent chemical analysis for years, utilization of this procedure to satisfy permit conditions is not a unique concept. Self-reporting provides the company with control of the treatment facility performance and the enforcement office with information on which discharge point needs investigation for possible permit violations.

SECTION IV

PARTICIPANT SELECTION

An inquiry was received from the Oklahoma Refiners Waste Control Council (ORWCC) expressing their concern of analytical variances experienced in analysing industrial wastewater samples at individual refineries. This organization, composed of 11 refinery members, has employed the self-reporting system for wastewater discharge analyses since 1955. Each month, the individual refineries report analytical data to the Oklahoma State Corporation Commission. Their selection as the participating industrial organization for this study insures the presence of laboratory experience in wastewater analyses, familiarity with analytical quality control procedures, and presence of the necessary laboratory supplies and equipment.

STEERING COMMITTEE

To attain the major and ancillary objectives of a study to define inter- and intralaboratory repeatability and reproducibility, a steering committee including one EPA, one state, and three refinery representatives was formed. Formation of the project plan was the responsibility of the committee while the liaison and project direction were responsibilities of Robert S. Kerr Environmental Research Laboratory (RSKERL) personnel. To prevent fragmentation of information relevant to project completion an organizational structure, such as the one used in this study shown in Figure 1, is a necessity for a project such as this involving multiple organizations.

The steering committee recommended four divisions for the analytical study: (1) low-level contamination wastewater analysis, (2) participant seminar to specify uniform procedures, (3) high-level contamination wastewater analysis, and (4) spike recovery from an industrial wastewater.

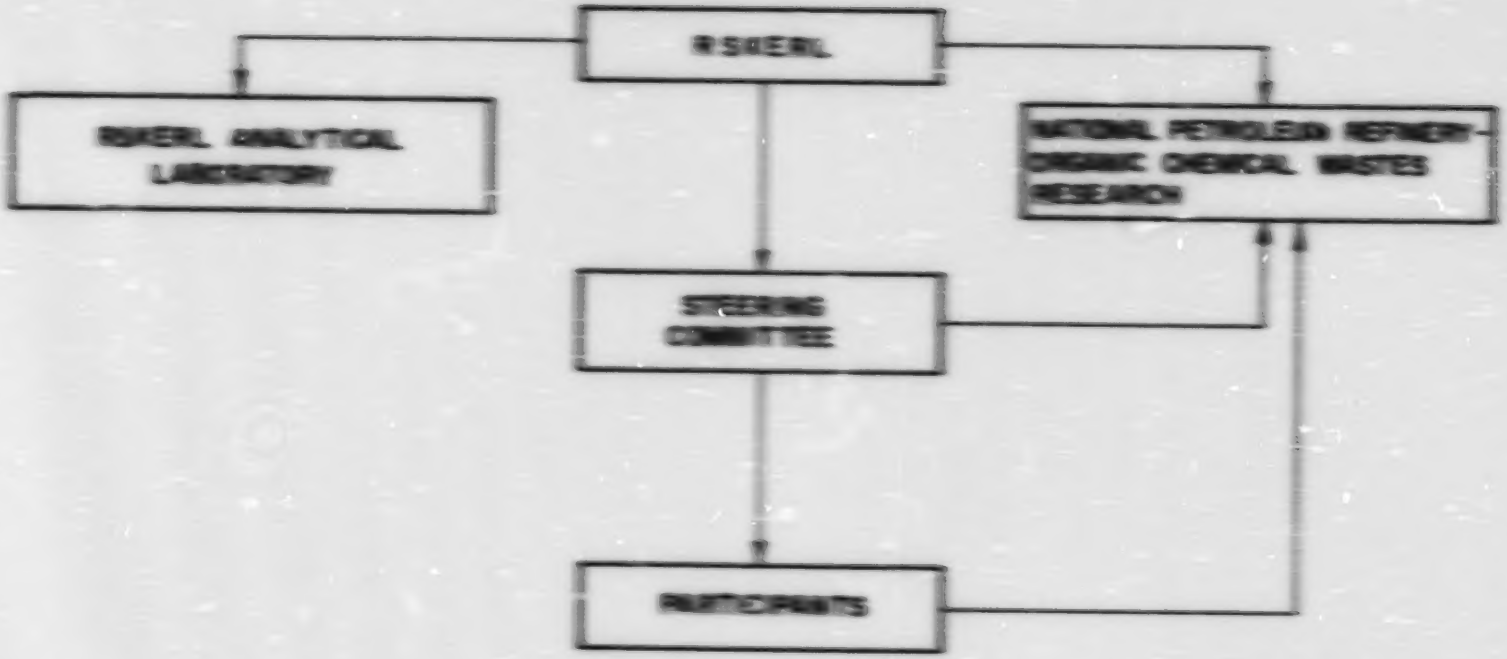

Figure 1. Project organizational structure

Participant selection from the council was voluntary, with the agreement that any refinery who volunteered would, of necessity, have to participate in the total program. Eight of the eleven member refineries agreed to participate in the project. Those refiners who did not choose to participate represent refineries who either contract their wastewater samples for analysis or could not participate due to internal restrictions. Refinery size of the participants varied from 12,000 to 112,000 barrels of crude per calendar day (MBCD). The size distribution of the participating refineries is shown in Table 1. Size variance of the participants is an important factor since the population (industrial participants) involved in the study should represent a spectrum from small to large. Refinery size also reflects laboratory capabilities for wastewater analyses since their analytical facilities are dependent on refinery size.

Two Oklahoma state agencies, which are currently involved in analysing industrial wastewaters, requested participation in the program. Those state agencies were the Oklahoma State Health Department, whose responsibilities include analyses of petroleum refinery wastewater for the

Table 1. CRUDE CAPACITY OF PARTICIPANTS

Refinery	Thousand Barrels/Calendar Day
A	12.0
B	25.0
C	38.5
D	39.5
E	48.5
F	51.0
G	87.0
H	112.0

Oklahoma Corporation Commission (Oklahoma's Enforcement Agency for petroleum refineries), and the Zoology Department of Oklahoma State University (OSU). The latter department has performed bioassays on petroleum refinery wastewaters since 1956 and regularly analyses refinery wastewaters.

EPA laboratories participating in the study were the RSKERL at Ada, Oklahoma, and the Methods Development and Quality Assurance Research Laboratory (MDQARL) located in Cincinnati, Ohio. MDQARL participation was primarily that of a referee laboratory while RSKERL duties included project liaison, sampling, intralaboratory analyses, data analyses, and report preparation. Related information and background including study schedule, laboratory equipment needed, correspondence relating to project liaison, report forms, and analytical instructions are located in Appendix A.

SECTION V

STUDY OBJECTIVE

The objective of this study was to observe the extent of analytical variability incurred for a specific industrial wastewater under controlled conditions for intralaboratory (repeatability), interlaboratory (reproducibility), and spike recovery.

Enforcement of the Federal Water Pollution Control Act (PL 92-500), which includes a self-reporting system, will be dependent on the precision and accuracy of the analytical results. Both parties in any court action should be prepared to furnish sufficient evidence that their analytical results are correct.

EPA's self-reporting system is based on two major variables: (1) analytical procedures, and (2) flow measurements. The basis of the reported values is:

$$\frac{\text{Discharge flow} \times \text{parameter concentration}}{\text{units of production}} \qquad (1)$$

This simple formula has two principal potential error sources: (1) analytical variability, and (2) flow measurement variability. For example, a 50,000 barrel per day (50 MBD) refinery which has a discharge flow of one million gallons per day (1 MGD) and a five-day biochemical oxygen demand (BOD_5) concentration of 30 mg/l may have a discharge load of 5.56 pounds per unit product.

$$\frac{30 \times 8.34 \times 1}{50} = 5.56 \text{ \#/MBD} \qquad (2)$$

If, because of analytical variability, the analyst reports 35 mg/l BOD_5, the discharge load would be 6.95 #/MBD which may constitute a permit violation. If, in the event of a flow metering error, which is quite

concern, a value of 1.2 MGD was used instead of 1.0 MGD, the example discharge load would be 6.67 #/MGD instead of 5.56 #/MGD. These sources of error are always present because of the technology and methodology involved in making the measurements.

Analytical variability, for the purposes of this study, is defined as the concentration differences reported by participating laboratories for a common industrial wastewater sample using a standardized testing procedure. Analytical variability is statistically measured by the standard deviation test.

Repeatability (precision) is defined as the variability encountered by a single analyst for the same sample analyzed with the same apparatus. The statistical measurement for repeatability is also the standard deviation test.

Reproducibility (precision) is defined as a measurement of the variability encountered in results from analysts from two or more laboratories for the same sample and is statistically evaluated using the standard deviation test procedure.

Spike recovery (accuracy) is a percentage measurement of the retrieval of a specified quantity of chemical added to the industrial wastewater.

SECTION VI

STUDY CONDITIONS

A list of factors which affect analytical variability was prepared as a guide to the study conditions. These analytical variation causes are listed below:

1. Analysts' laboratory techniques
2. Procedure alteration
3. Poor quality control
4. Improper standards
5. Poor reagents
6. Arithmetic errors
7. Poor sampling techniques
8. Improper equipment, supplies, and glassware
9. Interferences from other contaminents
10. Insufficient time allotted for proper analyses
11. Lack of explicit method

These factors may be summarily reduced to three items of principal concern: (1) sampling techniques, (2) interferences, and (3) laboratory factors.

To provide uniformity for the study, the following conditions were established prior to Phase I:

Sampling--A single industrial wastewater would be sampled and replicates divided among the participants.

Interfering Compounds--One sample set would not contain sulfide, while the other sample set would contain sulfide in sufficient concentration to cause interferences.

Analytical Procedure--The methods of choice to be followed would be EPA's "Methods for Chemical Analysis of Water and Wastes," 1971.[1]

Quality Control--Each participant was requested to use the "Laboratory Quality Control Manual," 1972.[2, 3]

Arithmetic Errors--A self-reporting format was to be provided for each analyst to submit necessary information to computer checking of calculations.

Analytical Techniques--Although the Phase I sample set would be analyzed in the stipulated manner, a participant seminar to provide additional information on techniques would be provided prior to Phase II sample set analyses.

Statistics--All data would be sent to the [illegible], Ada, Oklahoma, for statistical evaluation.

Parameters to be Determined--Parameters would include COD, phenolics, total suspended solids (TSS), ammonia nitrogen, and oil and grease. Those laboratories which had organic carbon instruments were requested to report total organic carbon (TOC).

Participants--Various industrial and enforcement laboratories would voluntarily participate. It was agreed to furnish each participant with a code identification.

"Spike" Sample--Certified "spike" samples prepared by EPA's [illegible], formerly Analytical Quality Control (AQC), would be included in each sample set for Phase I and II. Instructions for ammonia and COD spike additions were to be included with each sample set.

Referee laboratory services would be provided by the [illegible]. Inter-laboratory deviation would be determined at the [illegible] by analyzing six sample sets for each phase of the study. Participants were requested to begin analysis at specified times to insure uniformity of storage effect on analyses.

SECTION VII

SAMPLING PROCEDURES

Proper sampling of the industrial waste which was subdivided into 20 replicate samples was of utmost importance to the project. If any of the 20 samples were not representative, the project would be a failure from the beginning; unfortunately, there are not methods which can be used to obtain one truly representative grab sample, much less divide that one sample into 20 parts with the expectation that each of the 20 samples will be equal.

The sampling method used for the study involved centrifugally pumping the water at a medium volume rate (10 gallons per minute) into a 55-gallon drum which had an inert inner liner. Calculated amounts of preservatives were added to the sample and an electric mixer was used to mix the sample thoroughly. After five minutes of mixing, a replicate sample was withdrawn through a valve located near the bottom of the barrel into a previously numbered one-quart plastic or glass container. The numbered one-quart sample containers were filled at random to minimize the relation of the one-quart sample to the total volume in the 55-gallon drum. The samples were then placed into ice chests. A time interval of 15-20 minutes was needed to obtain each sample set. Upon completion of sample preparation for the five parameters, ice was placed in each chest to assist preservation of samples. A schematic of the sample equipment is depicted in Figure 2.

Various states of the sampling procedures were photographed for convenience of presentations.

Figure 3: Electric centrifugal pump installed on the clarifier catwalk with the intake pipe submerged about eight inches below the water surface. The discharge hose is directed to the sample barrel.

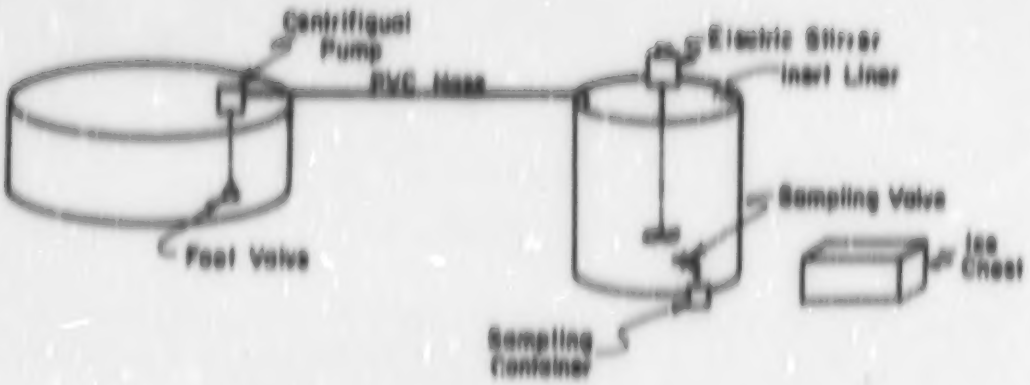

Figure 3. Equipment used to obtain representative sample

Figure 4: The inert lined sampling barrel being filled with wastewater to a pre-determined volume, as measured by depth. The electric stirrer was started after the correct sample volume was obtained and the preservative added.

Figure 5: Top view of the barrel shows the mixing pattern created by the electric stirrer. Continuous stirring was necessary to prevent settling of suspended solids and separation of oil which usually occur with refinery wastewaters.

Figure 6: Ice chests were arranged numerically and pre-numbered samples were placed in the box.

SAMPLE SETS

Sample volumes obtained and the preservative added for each sample set are shown in Table 3. Each sample set included 11 one-quart sample containers and the AQC samples for ammonia and COD spikes. Directions on analytical procedures and quality control were mailed prior to the sampling so the participants could correspond on problem areas. The project instructions and format for reporting analyses are located in Appendix A of this report.

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Figure 5. Top view of composite sampling container

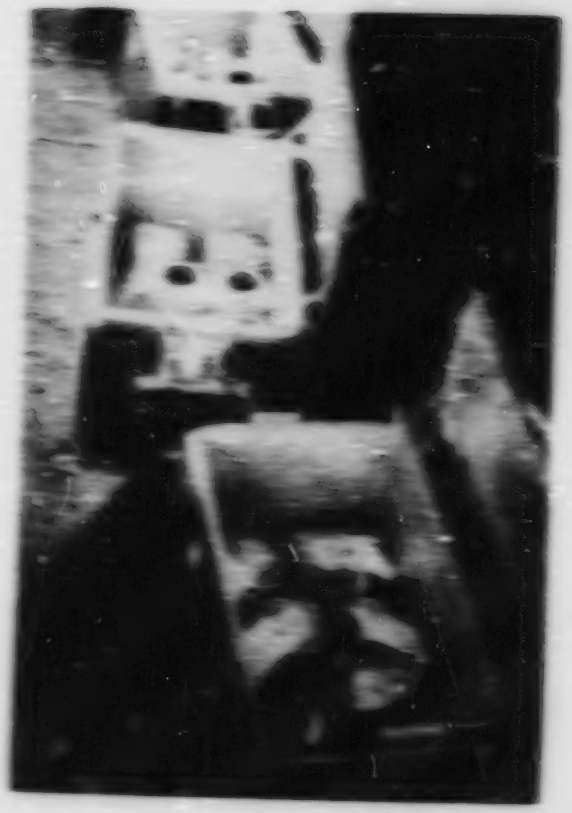

Figure 6. Sample sets for cooperative laboratories

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Table 2. SAMPLE VOLUMES AND PRESERVATIVES

Parameter	Barrel Vol. (gal.)	Preservative	Amount of Preservative	Vol. of sample Drawn/set
COD	17.0	Sulfuric Acid (conc)	136.0 ml	2 qts.
TSS	17.0	none	none	2 qts.
Ammonia	22.0	Mercuric Chloride	5.52 gm	3 qts.
Phenolics	22.0	Phosphoric Acid Copper Sulfate	304.0 ml 68.0 gm	3 qts.
Oil & Grease	17.0	Sulfuric Acid (conc)	40.0 ml	2 qts.

LOCATION OF SAMPLE POINTS

Wastewater for the first sample phase was obtained from a final clarifier at a petroleum refinery. The water had been biologically treated and represented all the water used in the refinery with the exception of sanitary sewage.

Wastewater for the second sampling phase was obtained from the discharge of an API type separator. This water was not biologically treated and contained sulfides which may cause interferences in analytical procedures.

SAMPLE DELIVERY

To insure uniformity of starting time, the participants were instructed to begin analyses at 10:00 a.m. (CST). Since the Phase I samples were obtained about 16 hours previous, the sample set could be air delivered to MDQARL, Cincinnati, Ohio. Due to unforeseen circumstances, the sample set was not delivered to MDQARL until the following day. A second sample set was analyzed by RSKERL at the later date for comparative purposes with the MDQARL samples.

The second phase sample set was delivered to the seminar participants. Initial analyses time was again set for 10:00 a.m. (CST). Correspondence with the involved airline insured sample receipt of the MDQARL samples on time.

SECTION VIII

PARTICIPANT SEMINAR

An instruction seminar, designed to furnish information on laboratory techniques, was presented to analysts participating in the study. A summary of the discussions is presented by parameter in Appendix B.

SAMPLE SET UNIFORMITY

Prime consideration was afforded the problem of obtaining 20 sample sets which contained virtually the same quantities of contaminants. As a preliminary screening device, TOC analysis was performed on suspended solid samples from six sample sets selected at random. Results of these analyses are listed in Table 5.

Results of this preliminary screening were sufficient to verify that uniformity of the 20 sample sets did exist, and that they were acceptable replicates.

Table 5. TOC ANALYSIS ON REPLICATE SAMPLES

Sample Set No.	TOC (mg/l)
01	23.0
03	23.0
07	23.0
09	23.0
14	23.5
18	23.5

SECTION IX

STATISTICAL EVALUATION

PRELIMINARY DATA CHECKING

Upon receipt of the completed data sheets from the various analysts and laboratories, an IBM 1130 computer was used to check each analysis for errors. When any error was detected, the mistake was either corrected or the analyst was contacted for an explanation, depending upon the nature and severity of the error. Whenever necessary the numerical value of each result was adjusted so that all the results could be represented with the identical number of decimal places.

OUTLIER REJECTIONS

All data were carefully reviewed and whenever appropriate, data points were rejected for the following reasons:

1. EPA analytical methodology was not used;
2. The analytical method used did not apply to the range of concentration in the sample;
3. The analyst reported the value as not reliable;
4. Statistical procedures revealed that the extreme values had only a small chance of validity and would make a significant change in the reported variability.

Outlier analyses proceeded in the following manner. Data which were rejected for reasons 1, 2, or 3 above were first culled. The extreme values were rejected by applying the two-tail "t" test to the remaining values at a 95 percent probability level; that is, with a 95 to 5 assurance that the data rejected were invalid and should be rejected. These values were probably caused by gross instrumental, chemical, or human error. In the Phase I study, 32 data points out of a total of

231 were rejected. In the Phase II study only five out of a total of 194 were rejected. The reduction in the amount of data rejected from the Phase I to Phase II indicates the effect of the instruction seminar.

DATA PRESENTATION

Tables 4 through 13 contain the results of the study with the data grouped according to source. Presented are the analytical results for each parameter for both phases of the study. The data analyzed at the RSKERL, Laboratory 01, are in one group and the results are a measure of the repeatability (intralaboratory variations). The data analyzed at the other laboratories are presented in the second group, and the results from this group are a measure of the reproducibility (interlaboratory variations). Also presented are the average results and standard deviations of the results from each group. Where applicable, the average spike recovery is presented. Also presented are the average results, standard deviation, and spike recovery for the data when both groups of data are combined.

DATA ANALYSES

Inter- vs Intralaboratory Variation

In order to statistically compare the results from the RSKERL and the other laboratories, the following analyses were carried out. The variance (σ^2) of the analytical data from both groups was compared by using the "F" test. The mean ($\bar{x}$) of the data from both groups was compared by use of the Student "t" test. Both of these tests were carried out at the 95 percent confidence level. The results are presented in Table 14 for both Phase I and Phase II.

As expected, the repeatabilities were smaller than the reproducibilities except for ammonia (Phase I), COD (Phase II), and oil and grease by the Hexane Method (Phase II). In these cases, there was no significant difference in the variabilities. In the case of ammonia analyses, there

were some instrumentation problems in Laboratory 01 which caused a higher than normal deviation. This problem was eliminated in Phase II. A comparison of oil and grease analysis for Phase I could not be made because of the limited amount of data available from Laboratory 01 for that test.

The normal expectation is that there should be no significant difference in the means of the two groups of laboratories. In this study, the only exceptions to this were for COD (Phase I), phenolics (Phase II), and oil and grease by the Freon method (Phase II). The instruction seminar held between Phase I and II may have improved the COD measurement. Phenolics and the Hexane oil and grease tests also improved but not to the same degree. The analytical methods may need revision for these two parameters.

Spike Recovery

The average spike recoveries in the Phase I study were 87.8 percent for COD and 22.1 percent for ammonia. In the Phase II the average spike recoveries were 95.1 percent for COD and 95.6 percent for ammonia. There was an obvious improvement in spike recovery as a result of the instruction seminar held between the two phases. This is particularly true for the ammonia test.

Oil and Grease Methods

A statistical evaluation was made to determine possible differences in the two oil and grease analytical methods. These results are presented in Table 15. A "t" test and "F" test were carried out at the 95 percent confidence level. The results indicate that there is no significant difference in the mean value of the two methods. However, it appears that the Freon method yields a lower standard deviation than does the Hexane method.

Table 4. COD ANALYTICAL METHOD EVALUATION - PHASE I
(Before Instruction)

Lab. No.	mg/l COD	mg/l Duplicate	mg/l Spiked	Spike Recovery (%)
Intralaboratory Results:				
01	77.6	77.6	106.1	92.2
01	77.6	79.6	106.1	89.0
01	76.3	75.5	102.0	84.5
01	83.7	75.5	104.1	79.5
01	77.6	77.6	108.2	99.0
01	75.5	75.5	102.0	92.2
	Average COD		= 77.1 mg/l	
	Standard Deviation		= 2.7 mg/l	
	Average Spike Recovery		= 89.4 percent	
Interlaboratory Results:				
02	71.0	82.8	110.4	108.4
05	91.8	95.3	125.8	104.5
08	78.1	78.1	106.9	93.2
10	89.0	85.0	125.5	134.6
11	87.6	83.7	115.5	96.8
13	74.0	82.2	98.6	66.5
15	122.9	119.0	-	-
16	145.0	145.0	164.0	61.9
17	59.0	59.0	83.0	77.7
20	111.7	121.4	131.5	48.5
	Average COD		= 94.1 mg/l	
	Standard Deviation		= 25.7 mg/l	
	Average Spike Recovery		= 86.8 percent	
Combined Results:				
	Average COD		= 87.7 mg/l	
	Standard Deviation		= 21.5 mg/l	
	Average Spike Recovery		= 87.8 percent	

Table 5. SUSPENDED SOLIDS ANALYTICAL METHODS EVALUATION - PHASE I (Before Instruction)

Lab. No.	Suspended Solids, mg/l	Duplicate
Intralaboratory Results:		
01	17.5	14.0
01	14.0	15.5
01	15.5	15.5
01	13.5	12.0
01	11.0	15.5
01	14.5	12.5
Average Suspended Solids = 13.8 mg/l		
Standard Deviation = 1.7 mg/l		
Interlaboratory Results:		
02	22.6	14.0
05	25.5	21.5
06	10.0	9.0
08	10.0	15.0
10	17.0	18.0
11	12.0	9.0
12	18.0	9.0
15	7.0	9.0
15	10.5	8.5
16	11.0	11.0
17	15.0	12.0
20	12.0	12.0
Average Suspended Solids = 13.2 mg/l		
Standard Deviation = 4.9 mg/l		
Combined Results:		
Average Suspended Solids = 13.4 mg/l		
Standard Deviation = 4.1 mg/l		

Table 6. AMMONIA ANALYTICAL METHOD EVALUATION - PHASE I
(Before Instruction)

Lab. No.	mg/l Ammonia	mg/l Duplicate	mg/l Spiked	Spike Recovery (%)
Intralaboratory Results:				
01	10.4	10.1	10.8	40.4
01	11.6	11.4	12.2	61.5
01	10.2	10.4	8.7	-117.6
01	12.6	12.6	13.8	88.2
01	12.1	12.4	13.7	106.6
01	12.4	12.2	13.8	88.3
01	12.6	12.4	13.8	85.6
	Average Ammonia	=	11.7 mg/l	
	Standard Deviation	=	1.0 mg/l	
	Average Spike Recovery	=	50.4 percent	
Interlaboratory Results:				
02	12.5	12.4	13.6	91.0
05	10.0	10.0	10.6	44.1
08	8.4	8.4	7.0	-102.0
10	12.4	12.4	13.6	88.2
11	12.1	11.9	13.2	88.2
13	14.0	11.2	5.6	-514.7
15	12.0	11.9	-	-
16	11.4	11.5	12.3	62.5
17	12.1	12.0	13.4	90.3
20	11.1	11.0	13.0	143.4
	Average Ammonia	=	11.4 mg/l	
	Standard Deviation	=	1.4 mg/l	
	Average Spike Recovery	=	0.0 percent	
Combined Results:				
	Average Ammonia	=	11.5 mg/l	
	Standard Deviation	=	1.2 mg/l	
	Average Spike Recovery	=	22.1 percent	

Table 7. PHENOLICS ANALYTICAL METHOD EVALUATION - PHASE I
(Before Instruction)

Lab. No.	Phenolics µg/l	Duplicate
Intralaboratory Results:		
01	15.0	11.3
01	14.4	11.5
01	9.7	10.3
01	14.0	11.2
01	15.9	11.7
01	15.9	9.8
01	15.5	10.8
Average Phenolics =	12.2 µg/l	
Standard Deviation =	1.8 µg/l	
Interlaboratory Results:		
02	14.0	15.0
05	24.0	21.9
08	5.5	4.0
10	20.0	17.0
11	29.3	29.0
13	4.0	4.0
16	15.6	20.7
17	12.5	5.8
20	12.0	15.0
Average Phenolics =	15.2 µg/l	
Standard Deviation =	8.1 µg/l	
Combined Results:		
Average Phenolics =	13.9 µg/l	
Standard Deviation =	6.5 µg/l	

Table 8. OIL AND GREASE METHOD EVALUATION - PHASE I
(Before Instruction)

Lab. No.	Hexane	Duplicate	Freon	Duplicate
		mg/l		
Combined Results:				
01	4.7	"	5.1	"
02	4.5	"	2.8	"
06	"	"	6.4	5.4
08	6.8	8.7	"	"
10	6.4	"	6.5	"
11	"	"	6.1	5.4
13	4.5	5.5	"	"
15	9.9	8.5	"	"
16	4.9	"	6.5	"
17	"	"	5.5	5.8
20	"	"	5.6	4.0
Average Hexane			"	6.5 mg/l
Standard Deviation Hexane			"	2.0 mg/l
Average Freon			"	4.9 mg/l
Standard Deviation Freon			"	1.3 mg/l
Average Oil and Grease			"	5.6 mg/l
Standard Deviation Oil and Grease			"	1.8 mg/l

Table 9. COD ANALYTICAL METHOD EVALUATION - PHASE II
(After Instruction)

Lab. No.	mg/l COD	mg/l Duplicate	mg/l Spiked	Spike Recovery (%)
Intralaboratory Results:				
01	125.5	125.5	485.8	97.4
01	138.2	138.2	503.0	98.8
01	142.3	146.5	503.9	106.9
01	146.5	146.5	485.8	94.5
01	125.5	125.5	485.8	97.4
01	125.5	125.5	485.8	97.4
	Average COD	=	134.2 mg/l	
	Standard Deviation	=	9.5 mg/l	
	Average Spike Recovery	=	98.7 percent	
Interlaboratory Results:				
03	127.5	135.5	474.1	92.6
05	130.3	130.3	456.1	88.1
06	116.0	121.0	423.4	82.3
08	150.3	142.3	505.9	97.2
10	119.5	119.5	478.1	96.9
11	144.0	140.0	5[illegible].0	98.9
15	143.9	143.9	505.7	97.2
16	172.7	168.7	494.0	87.4
17	139.4	151.4	498.0	95.5
20	142.6	142.6	487.8	93.5
	Average COD	=	139.1 mg/l	
	Standard Deviation	=	15.0 mg/l	
	Average Spike Recovery	=	92.9 percent	
Combined Results:				
	Average COD	=	137.3 mg/l	
	Standard Deviation	=	13.3 mg/l	
	Average Spike Recovery	=	95.1 percent	

Table 10. SUSPENDED SOLIDS ANALYTICAL METHOD EVALUATION - PHASE II (After Instruction)

Lab. No.	Suspended Solids mg/l	Duplicate
Intralaboratory Results:		
01	17.5	14.5
01	21.5	20.5
01	19.0	19.0
01	20.5	18.5
01	20.0	19.5
01	20.5	20.0
Average Suspended Solids	=	19.5 mg/l
Standard Deviation	=	1.8 mg/l
Interlaboratory Results:		
02	18.2	19.1
05	22.5	23.2
06	16.0	15.0
08	17.0	16.0
10	20.0	19.5
11	19.0	21.0
12	0.0	5.5
15	19.5	19.5
16	19.0	18.0
17	20.0	22.0
20	15.0	17.0
Average Suspended Solids	=	18.2 mg/l
Standard Deviation	=	5.3 mg/l
Combined Results:		
Average Suspended Solids	=	18.6 mg/l
Standard Deviation	=	4.3 mg/l

Table 11. AMMONIA ANALYTICAL METHOD EVALUATION - PHASE II
(After Instruction)

Lab. No.	mg/l Ammonia	mg/l Duplicate	mg/l Spiked	Spike Recovery (%)
Intralaboratory Results:				
01	8.7	8.8	18.3	96.8
01	8.7	8.7	18.4	98.6
01	8.6	8.7	18.4	97.8
01	8.7	8.9	18.4	97.1
01	8.8	8.8	18.4	97.1
01	8.7	8.6	18.3	97.8
	Average Ammonia	=	8.7 mg/l	
	Standard Deviation	=	0.1 mg/l	
	Average Spike Recovery	=	97.4 percent	
Interlaboratory Results:				
02	8.5	8.4	14.0	96.3
05	7.6	7.6	14.1	95.6
08	7.0	5.6	11.2	72.1
10	8.7	8.7	16.1	94.1
11	8.5	8.5	14.8	92.6
12	8.4	8.5	16.5	118.4
15	9.2	9.1	18.3	90.4
16	9.5	9.2	14.3	89.0
17	9.1	9.2	16.4	106.6
20	9.4	9.1	18.4	90.4
	Average Ammonia	=	8.5 mg/l	
	Standard Deviation	=	0.9 mg/l	
	Average Spike Recovery	=	94.6 percent	
Combined Results:				
	Average Ammonia	=	8.6 mg/l	
	Standard Deviation	=	0.7 mg/l	
	Average Spike Recovery	=	95.6 percent	

Table 14. PHENOLICS ANALYTICAL METHOD EVALUATION - PHASE II
(After Instruction)

Lab. No.	Phenolics, µg/l	Duplicate
Intralaboratory Results:		
01	5480	5367
01	5170	5500
01	5480	5150
01	5320	5367
01	5320	5285
01	6070	4800
Average Phenolics =	5300.6 µg/l	
Standard Deviation =	306.5 µg/l	
Interlaboratory Results:		
02	5338	6088
05	6600	6720
08	6600	5000
10	4250	4460
11	6150	6200
16	5400	5500
17	5100	5200
20	6080	6550
Average Phenolics =	5761.0 µg/l	
Standard Deviation =	795.8 µg/l	
Combined Results:		
Average Phenolics =	5563.7 µg/l	
Standard Deviation =	650.4 µg/l	

Table 13. OIL AND GREASE METHOD EVALUATION - PHASE II
(After Instruction)

Lab. No.	mg/l Hexane	Duplicate	Freon	Duplicate
Interlaboratory Results:				
01	11.8	"	12.0	"
01	8.3	"	"	"
01	10.8	"	12.4	"
01	7.1	"	11.7	"
01	4.8	"	10.5	"
01	10.0	"	11.4	"
Average Hexane = 8.0 mg/l				
Standard Deviation Hexane = 2.5 mg/l				
Average Freon = 11.6 mg/l				
Standard Deviation Freon = 0.7 mg/l				
Average Oil and Grease (both methods) = 10.1 mg/l				
Standard Deviation Oil and Grease (both methods) = 3.5 mg/l				
Interlaboratory Results:				
02	10.4	9.7	10.9	11.0
06	"	"	8.5	7.4
08	8.9	10.6	"	"
10	10.4	"	"	10.5
11	"	"	13.5	14.4
12	11.3	12.4	"	"
15	10.4	"	"	"
16	15.1	"	"	"
17	17.9	19.3	"	"
20	"	"	10.8	11.6
Average Hexane = 12.5 mg/l				
Standard Deviation Hexane = 3.4 mg/l				
Average Freon = 10.9 mg/l				
Standard Deviation Freon = 2.0 mg/l				
Average Oil and Grease (both methods) = 11.8 mg/l				
Standard Deviation Oil and Grease (both methods) = 3.9 mg/l				
Combined Results:				
Average Hexane = 11.4 mg/l				
Standard Deviation Hexane = 3.5 mg/l				
Average Freon = 11.1 mg/l				
Standard Deviation Freon = 1.7 mg/l				
Average Oil and Grease (both methods) = 11.2 mg/l				
Standard Deviation Oil and Grease (both methods) = 3.8 mg/l				

Table 14. STATISTICAL COMPARISON OF LABORATORY 01 WITH THE OTHER LABORATORIES (at the 95% confidence level)

Analysis	Variance, s^2		Mean, $\bar{x}$	
	F Value	Statistically Significant[a]	t Value	Statistically Significant[b]
Phase I:				
COD	84.80	Yes	3.97	Yes
Solids	8.60	Yes	0.52	No
Ammonia	1.00	No	0.60	No
Phenolics	19.08	Yes	1.81	No
Phase II:				
COD	3.48	No	1.13	No
Solids	7.99	Yes	0.85	No
Ammonia	157.00	Yes	1.25	No
Phenolics	14.80	Yes	2.22	Yes
Oil and Grease - Hexane	1.76	No	3.40	Yes
Oil and Grease - Freon	8.14	Yes	0.92	No

[a] If the "F" value is statistically significant (Yes), this indicates that the interlaboratory deviation is larger than the intralaboratory deviation. Normally it is expected that the "F" will be significant. Exceptions noted are: Ammonia (Phase I), COD (Phase II), Oil and Grease - Hexane (Phase II).

[b] If the "t" value is statistically significant (Yes), this indicates that the average results from Laboratory 01 are different from those of other laboratories. Cases where the means are different are: COD (Phase I), Phenolics (Phase II), Oil and Grease - Hexane (Phase II).

Table 15. STATISTICAL COMPARISON OF THE HEXANE AND FREON METHODS FOR THE ANALYSIS OF OIL AND GREASE (at the 95% confidence level)

Phase	Variance of		Mean X	
	F Value	Statistically Significant	t Value	Statistically Significant
I	2.10	No	2.15	No
II	4.24	Yes	0.11	No

SECTION 8

REFERENCES

1. Analytical Quality Control Laboratory. Methods for Chemical Analysis of Water and Wastes, 1971. U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-16010---07/71. July 1971.

2. Analytical Quality Control Program. Laboratory Quality Control Manual, 2nd Edition. U.S. Environmental Protection Agency, Ada, Oklahoma. 1972.

3. Analytical Quality Control Laboratory. Analytical Quality Control in Water and Wastewater Laboratories. U.S. Environmental Protection Agency, Cincinnati, Ohio. June 1972.

SECTION XI
APPENDICES

Appendix		Page
A	Related Information and Background	57
	Study Schedule	57
	Laboratory Equipment Needed	43
	Correspondence Relating to Project Liaison	46
	Report Forms	52
	Analytical Instructions	59
B	Seminar Summary	61
	Chemical Oxygen Demand	61
	Total Suspended Solids	62
	Distillation of Ammonia Procedure	62
	Phenolics	63
	Oil and Grease	63

APPENDIX A

RELATED INFORMATION AND BACKGROUND

STUDY SCENARIO

Purpose of Study

To scientifically determine the repeatability and reproducibility of quantitatively measuring amounts of impurities in petroleum refining wastewaters.

Participants in Study

Through the years an excellent working relationship has been established between the RSKERL and ORNCC on refinery waste treatment research studies. The participants will be the member refineries, the RSKERL, and the MDQARL, which will provide referee laboratory service during the entire study.

Study Program

Split samples will be preserved and sent to the participants for their analyses. There will be three samples to be analyzed: (1) Low Level Sample (2) Low Level Sample, and (3) EPA Analytical Quality Control Sample. On receipt of the first sample set, the analyst will add the AQC sample (3) to the (2) sample. This sample will be referred to as the spike sample. Specific instructions will be sent with the sample set.

Analytical procedures must be run according to the EPA methodology. If additional procedures are used for analyses, a reference to that procedure should be recorded.

To facilitate analytical expediency, a range of concentrations will be supplied with each sample similar to the illustration below.

SAMPLE #1

Range (mg/l)	Parameter	Procedure	Page
40-150	Chemical Oxygen Demand	High Level	24-28
.01-.5	Phenolics	4-AAP	252-254
5-25	Oil and Grease	Hexane Ext.	217-220
20-50	Ammonia Nitrogen	Distillation Proc.	154-160
15-40	Total Suspended Solids	Non-Filterable	278-279

Analyses will be performed for chemical oxygen demand, phenolics, oil and grease, ammonia nitrogen and total suspended solids by the participating laboratories.

Each participant's analysis will be returned to the RSKERL where compilation and statistical analyses will be performed on the data.

Training Symposium

To provide analytical uniformity for the second set of samples, a seminar will be held at the RSKERL in February. At this seminar, the chemists and technicians, who will be analysing the second set of samples, will receive specific instruction on procedure and analytical techniques. The seminar will be presented on the first day, and a set of samples will be analysed by the participants on the second day. The second set of samples will be delivered the following week.

It would be desirable if the EPA quality control procedures were followed during both testing exercises. If, for some reason, this cannot be done on the first sample set, it should be so noted. To maintain uniformity, quality control has to be done on the second sample set.

For your information, Figures 7-11 are photographs typical of each set-up. Laboratory equipment needed with cost data of the set-up is also provided. If you do not have the equipment, you may consider ordering it from a supplier.

Figure 7. [illegible]

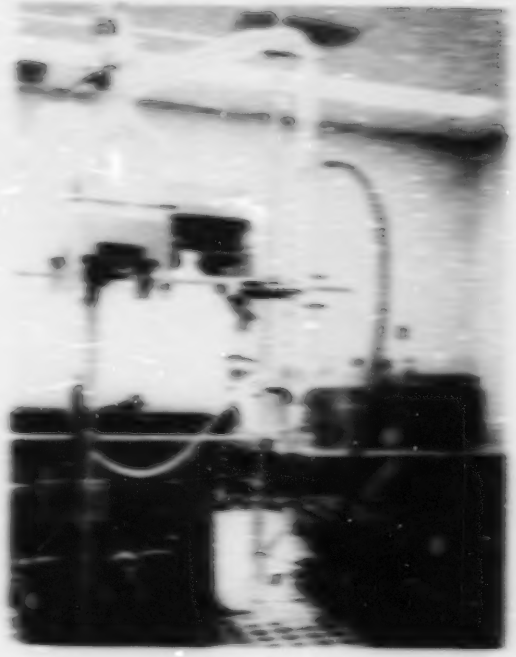

Figure 8. [illegible]

Figure 9. Oil and grease [illegible] sump

Figure 10. [illegible]

Figure 11. Suspended solids set-up

Sampling Dates

It is anticipated the first sampling will be done on January 15; the training symposium on February 5; and the second sampling on February 15. The results of the survey will be available by April 1.

Study Outline

Date	Event
December 1973	
5	EPA ORNEC Committee Meeting
6	Presentation of Study to Members
15	Concurrence of Participants
18	Study Profile Mailed to Participants
January 1974	
15	Sample Collected
15	Sample Transferred to Participants
15	Analysis Performed
18	Sample Data Sent to ESEERL
23	Data Summary Sent to Participants
30	Committee Meeting for Second Phase
February 1974	
5	Training Seminar
15	Second Set of Sample
15	Analysis Performed
15	Data Sent to ESEERL
20	Data Summary Sent to Participants
27	Committee Meeting
March 1974	
15	First Draft Report
25	Rewrite
April 1974	Present to ORNEC at OSU

LABORATORY EQUIPMENT NEEDED

	Equipment	Cost
Chemical Oxygen Demand:		
1.	Reflux apparatus 500 ml Erlenmeyer flask with 24/40 standard taper joint	$ 5.00
	or 500 ml boiling flask with 24/40 STJ	5.34
2.	Allihn condenser with 24/40 STJ at bottom, 12" or equivalent	13.00
	or Freidrichs condenser with 24/40 STJ at bottom	16.53
3.	1 - 25 ml burets (teflon plug)	12.00
4.	Assorted pipets	
5.	Glass beads	
Oil and Greases:		
1.	Soxlet extractor (Corning 3740 or equivalent) medium	21.00
2.	Soxlet thimbles to fit extractor (33x80) fat free (box of 25)	6.00
3.	Flask 125 ml Corning No. 4100 or equivalent	5.75
4.	Allihn condenser (bulb type) to fit extractor with 45/50 STJ bottom	
5.	Source of vacuum	
6.	Buchner funnel 12 cm or on which will accept	13.00
7.	Filter paper - Whatman No. 40 or equivalent 11 cm (pkg. 100)	2.11
8.	Muslin cloth discs 11 cm (cut from muslin bought at drygoods store)	
9.	Filter flask to fit buchner Funnel 1000-2000 ml	8.00
10.	Stopper to adapt funnel to filter flask	.50
11.	Filter aids (Hyflo Super-cel) - John Manville Corp. or equivalent - 1 lb.	2.25
12.	Oven set for 103° C	

13.	Water bath (may be made)	130.00-250.00
14.	Steam bath	150.00-200.00
15.	Glass beads	
16.	Source of heat for extraction steam bath or standard method advocates a heating mantle for flask, etc.	Price will depend on heat source.
17.	Balance (analytical)	250.00-1000.00
18.	Dessicator for drying + plate (price varies)	approx. 10.00

Ammonia Nitrogen:

All glass distillation apparatus with 500-1000 ml flask or Kjeldahl distillation rack. The phenol distillation equipment may be used. (For price see Phenol) If phenol distilling units are used, ignore 3, 4, and 5.

1.	Titration setup utilising a buret or the colorimetric test utilising nessler tubes and a spectraphotometer. Colorimetric should be utilised for low levels.	
2.	Nessler tubes (Full form, 50 ml)	each 2.50
3.	Kjeldahl distilling rack (2 units)	300.00-400.00
4.	Kjeldahl Flask 500-1000 ml	6 for 15.00
5.	Kjeldahl bulb, Iowa State type or equivalent	each 5.00
6.	Erlenmeyer Flasks (500 ml) glass stoppered	each 5.00
7.	Various standard lab glassware	

Phenol:

1.	Distilling apparatus with Graham condenser, Corning No. 5360 or equivalent 1000 ml	each 29.80
2.	1000 ml beakers	approx. 2.00
3.	pH meter	
4.	500 ml graduated cylinders or 500 ml volumetric Flasks	9.00 5.00
5.	Photometric equipment for work @ 460 mμ	various prices
6.	Filter paper 11 cm	approx. 2.00
7.	Separatory funnels 1000 ml Squibb form with ground glass stoppers and teflon stopcocks	15.00

8. Nessler tubes 50 ml tall form (matched) 2.50

9. Buret 10 ml 20.00

10. Balance (see Oil and Greases)

11. Various common lab glassware, such as pipets, etc.

Solids, Non Filterable - Suspended:

1. Glass fiber filter discs, 4.7 cm or 2.2 cm without organic binder. Reeve Angel type 934-H or 984-H, Gelman type A, or equivalent.

2. Filter holder, membrane filter funnel or Gooch crucible adaptor.

3. Suction flask 500 ml approx. 7.00

4. Gooch crucibles 25 ml if 2.2 cm filter used 1.40

5. Drying oven 103°-105° C price varies 80.00-500.00

6. Desiccator depends on size, approx. 20.00

7. Analytical balance 200 g. capacity price varies 800.00-1000.00 capable of weighing to 0.1 mg. (An automatic, such as Mettler or equivalent)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
P. O. BOX 1198
ADA, OKLAHOMA 74820

January 18, 1974

Dear Participant:

On January 29 the first samples for the Round Robin Study will be distributed to the various participating laboratories.

All samples should be delivered in time to begin the analyses by 11:00 a.m. at the latest.

The samples will consist of:

1. A petroleum refinery effluent which has been sampled in a manner which should produce comparable analytical results on all parameters.

2. A duplicate of No. 1 which should be run to satisfy data requirement concerning the reproducibility of results within a given laboratory.

3. A duplicate of No. 1 which will receive a spike or addition of a standard substance to test for interferences in the refinery effluent.

The samples are to be run for: (a) suspended solids or non-filterable solids, (b) phenols, (c) ammonia-N, (d) chemical oxygen demand, and (e) oil and grease.

Each sample will be appropriately preserved and will be tagged to indicate the proper analysis.

At the present time, it is feasible to spike the samples for only ammonia-N and chemical oxygen demand, thus these will be the only two analyses which will be required on the spiked samples.

The samples and number of analyses to be performed are:

Set No. 1

No. S (Lab No.) L refinery effluent for suspended solids	= 1
No. P (Lab No.) L refinery effluent for phenol	= 1
No. N (Lab No.) L refinery effluent for ammonia-N	= 1
No. C (Lab No.) L refinery effluent for COD	= 1
No. O (Lab No.) L refinery effluent for oil and grease	= 1
Total Analyses	5

Set No. 2

No. S (Lab No.) D duplicate refinery effluent for suspended solids	= 1
No. P (Lab No.) D duplicate refinery effluent for phenol	= 1
No. N (Lab No.) D duplicate refinery effluent for ammonia-N	= 1
No. C (Lab No.) D duplicate refinery effluent for COD	= 1
No. O (Lab No.) D duplicate refinery effluent for oil and grease	= 1
Total Analyses	5

Set No. 3

No. N (Lab No.) S duplicate refinery effluent and spike for ammonia-N	= 1
No. C (Lab No.) S duplicate refinery effluent and spike for COD	= 1
Total Analyses	2

The methods to be used will be found in the EPA manual "Methods for Chemical Analysis of Water and Wastes," 1971, which you should have already received. As a suggestion, the parameters and applicable tests would be:

Phenols - EPA Manual, page 332 - use procedure of Standard Method 13th Edition beginning on page 502 with distillation and use chloroform extraction, pages 504 through 506.

Suspended Solids - EPA Manual, pages 278 through 279.

Ammonia-N - EPA Manual, pages 134 through 140 beginning distillation and using either the titration or the colorimetric procedures. (The RSKERL plans to use the titration procedure.)

Oil and Grease - The Freon (trichlorotrifluoroethane) extraction method of Standard Methods 13th Edition, page 354 is recommened unless reagents and glassware are not available. Hexane extraction should be the next choice, EPA Manual, pages 317 through 320. If possible, do one oil and grease sample by each method.

Chemical Oxygen Demand - EPA Manual, page 19, gives the low level procedure. It is advised that the test prescribed is Standard Methods, pages 495 through 499, using the higher normality dichromate and ferrous ammonium sulfate be the method of choice for the samples which we will be analysing.

Instructions for Chemical Oxygen Demand Spike of Refinery Effluent

A vial of concentrate will be received with the set of samples to be run for the Round Robin Study.

The demand concentrate is prepared by dissolving known amounts of analytical reagent-grade glucose and glutamic acid in distilled water. Each concentrate can be analysed for biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). COD is the only analysis we are requesting at this time, however.

When diluted according to instructions, the COD of the sample will be increased in the range of 0 to 50 mg/l.

The concentrate has been preserved by autoclaving the sealed ampul, after which repeated analyses over a period of weeks by the Analytical Quality Control Laboratory of EPA located at Cincinnati, Ohio, were conducted to insure stability of the concentrate. However, the concentrate must be diluted and analysed immediately after the ampul is opened to avoid degradation of the compounds.

When you are ready to begin the analysis, open the ampul by snapping the top off at the break area on the neck and dilute with the No. C (Lab No.) 8 refinery effluent as follows: Dilute 15 ml of concentrate 1 to volume in a 500 ml volumetric flask with the refinery effluent.

The analysis for COD may now be carried out as described in the EPA Manual and Standard Methods 13th Edition.

Instructions for Ammonia-N Spike of the Refinery Effluent

A vial of concentrate will be received with the set of samples to be run for the Round Robin Study.

The concentrate is prepared by dissolving known amounts of analytical grade chemicals in distilled water for exact and pre-planned concentrations. When diluted according to instructions, the concentration of ammonia-N added to the sample will fall within the range of less than 3 mg/l as NH_3-N.

Each sample will be analysed at least six times at the RSKERL to determine variation.

The Analytical Quality Control Laboratory of EPA, located at Cincinnati, Ohio, who prepares these standards, has repeatedly analysed the standards over a period of months to assure stability.

The first vial you recieve will be designated Concentrate I Nutrients, and will contain inorganic nitrogen and phosphorus forms. Laboratories interested in their accuracy in analysing for nitrate-N and orthophosphate can utilise the concentrate to investigate these values as well. Analysis for ammonia-N is the only analysis we are specifying at this time, however. The range for nitrate-N will fall below 2.0 mg/l and orthophosphate as P will be below 1.0 mg/l for those who are interested.

All constituents are present in a soluble form. Do not filter the concentrates. They have been preserved so that no changes will occur, however, the preservative treatment is not effective after dilution. Therefore, the samples must be analysed immediately after opening and diluting.

To begin the analysis, open the ampul by snapping the top off the scored break area on the neck and dilute a 10 ml aliquot of the concentrate to 500 ml with the refinery effluent specified for ammonia-N analysis spike (No. N (Lab No.) 5). Approximately 25 ml of the concentrate is supplied. The 500 samples may now be analysed for ammonia nitrogen as requested.

Yours truly,

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
P. O. BOX 1198
ADA, OKLAHOMA 74820

January 28, 1974

Dear Participant:

You will find attached to this letter several blank forms for reporting the following analyses:

1. Chemical oxygen demand - 8 copies
2. Suspended solids - 8 copies
3. Oil and grease (Hexane) - 8 copies
4. Oil and grease (Freon) - 8 copies
5. Ammonia (Spectrophotometric) - 8 copies
6. Ammonia (titrimetric) - 8 copies
7. Phenolics - 4 copies

We would like to request that you use these forms in reporting the results of your laboratory's analyses. Your cooperation will greatly facilitate the statistical analyses of the results. One form should be completed for each sample analyzed. (There will be an excess of oil and grease and ammonia forms as there are two methods for running both of these analyses.)

Each form will request the following information:

Storet Number - Already filled in on the form.

Laboratory Code - Already filled in on the form.

Date - The date this analysis was started. Please use the following format: 01/29/74 for January 29, 1974.

Sample Number - As printed on the sample tag and container. An example of a sample number is O-25-L. The first letter of the sample number signifies the analysis. O is for oil and grease, N is for ammonia, P is for phenol, C is for COD, and S is for solids. The second set of digits is the laboratory code. The last letter will be either L, D, or S. Sample numbers ending with "S" are to be spiked.

Time at Start of Analysis - Please use military time (1500 for 1:00 p.m.)

Time at Completion of Analysis - Military time. If the analysis is completed on a day other than the starting date, please make note of this in the comments section.

Is Sample Spiked - Check yes or no.

Method Number - Already filled in on the form.

Analytical Results - Detailed information is requested for each analysis. This will help verify the results. Completion of this section will eliminate possible questions about simple arithmetic errors and will provide a complete record of the test.

Comments - Any additional information that the analyst desires to report.

Analyst's Initials

The samples in this study will be taken from a refinery waste stream. We expect the analyses of this stream to fall within the following ranges:

Ammonia	10 - 30 mg/l
COD	75 - 135 mg/l
Phenolics	0.05 - 0.3 mg/l
Suspended Solids	20 - 40 mg/l
Oil and Grease	5 - 25 mg/l

As this waste stream varies from day to day, we cannot be certain that the results will always fall within this range.

Please use the enclosed self-addressed envelope to return your results. We would appreciate it very much if you could mail out the results by February 1, 1974.

Yours very truly,

Enclosures

CHEMICAL OXYGEN DEMAND
ANALYSIS SHEET

Stored Number: 00555

Laboratory Code: 16

Date: _____

Sample Number: _____

Time at Start of Analysis: _____

Time at Completion of Analysis: _____

Is the Sample Spiked: Yes___ No___

Method Number: 1

Analytical Results:

Normality of $K_2Cr_2O_7$ _____N

mls $K_2Cr_2O_7$ for normality titrations _____mls

mls Fe $(NH_4)_2$ $(SO_4)_2$ used for normality titrations _____mls

Normality Fe $(NH_4)_2$ $(SO_4)_2$ =

$$\frac{\text{mls } K_2Cr_2O_7 \times (\text{Normality } K_2Cr_2O_7)}{\text{mls Fe } (NH_4)_2 (SO_4)_2 \text{ Used}} = \text{_____N}$$

mls $K_2Cr_2O_7$ used in test _____mls

mls sample used _____mls

mls Fe $(NH_4)_2$ $(SO_4)_2$ used in blank titration _____mls

ml Fe $(NH_4)_2$ $(SO_4)_2$ used in sample titration _____mls

mg/l COD = [(mls Fe $(NH_4)_2$ $(SO_4)_2$ for blank - mls Fe $(NH_4)_2$ $(SO_4)_2$) x (N of Fe $(NH_4)SO_4)_2$ x 8000)] ÷ mls of sample used = _____mg/l

Comments:

Analyst's Initials _____

NON-FILTERABLE (SUSPENDED) SOLIDS
ANALYSIS SHEET

Storet Number: 00530

Laboratory Code: 10

Date: _____

Sample Number: _____

Time at Start of Analysis: _____

Time at Completion of Analysis: _____

Is the Sample Spiked: Yes___ No___

Method Number: 1

Analytical Results:

Volume Filtered _____ ml

Dried weight of crucible, mat, and residue _____ gms

Dried weight of crucibles and mat _____ gms

Weight of residue _____ gms

mg/l suspended solids =

$$\frac{\text{weight residue} \times 1{,}000{,}000}{\text{Volume Filtered}} = \text{_____ mg/l}$$

Comments:

Analyst's Initials _____

OIL AND GREASE BY HEXANE EXTRACTION
ANALYSIS SHEET

Stored Number: 00550

Laboratory Code: 16

Date: _____

Sample Number: _____

Time at Start of Analysis: _____

Time at Completion of Analysis: _____

Is the Sample Spiked: Yes___ No___

Method Number: 1

Analytical Results:

Volume of sample used _____ mls

Weight of flask and oil _____ grams

Tare weight of flask _____ grams

Weight of oil _____ grams

$$mg/l \text{ of oil} = \frac{(\text{gms of oil}) \times 1{,}000{,}000}{\text{mls of sample}} = \text{_____ mg/l}$$

Comments:

Analyst's Initials _____

OIL AND GREASE BY FREON EXTRACTION
ANALYSIS SHEET

Storet Number: 00550

Laboratory Code: 16

Date: _____

Sample Number: _____

Time at Start of Analysis: _____

Time at Completion of Analysis: _____

Is the Sample Spiked: Yes___ No___

Method Number: 1

Analytical Results:

Volume of sample used _____ ml

Weight of flask + residue _____ gms

Weight of flask _____ gms

Weight of material found in blank run on solvent. (The same amount of solvent used as sample is placed in a tared flask and evaporated. The increase in wt. constitutes a blank.) _____ gms

mg/l oil or grease = $\frac{[(\text{Flask + residue}) \text{ gms} - (\text{wt. flask}) \text{ gms} - \text{wt. blank, gms}] \times 1{,}000{,}000}{\text{ml sample}}$ ___ ___ mg/l

Comments:

Analyst's Initials _____

AMMONIA NITROGEN
(Spectrophotometric Procedure)
ANALYSIS SHEET

Storet Number: 00610

Laboratory Code: 16

Date: _____

Sample Number: _____

Time at Start of Analysis: _____

Time at Completion of Analysis: _____

Is the Sample Spiked: Yes___ No___

Method Number: 2

Analytical Results:

Volume of the 500* mls of distillate which is Nesslerized. _____mls

Standard Curve:	mg NH_3-N/l	Optical Density (Absorbance)
	_____	_____
	_____	_____
	_____	_____

Optical density (absorbance) for sample mg NH_3-N from standard curve. _____mg/l

$$\text{mg/l ammonia-N} = \frac{(\text{mg } NH_3\text{-N/l}) \times 1000}{.8 \times \text{Volume Nesslerized}} = \text{_____mg/l}$$

Comments:

Analyst's Initials _____

*Use 400 ml of sample, distill and dilute to 500 ml. This is the distillate.

AMMONIA NITROGEN
(Titrimetric Procedure)
ANALYSIS SHEET

Storet Number: 00610

Laboratory Code: 10

Date: _____

Sample Number: _____

Time at Start of Analysis: _____

Time at Completion of Analysis: _____

Is the Sample Spiked: Yes__ No__

Method Number: 1

Analytical Results:

Volume of sample distilled _____ mls

Volume of 0.01 N H_2SO_4 used _____ mls

$$mg/l \text{ ammonia} = \frac{(\text{mls of } H_2SO_4) \times .14 \times 1000}{(\text{mls of sample})} = \text{_____ mg/l}$$

Comments:

Analyst's Initials _____

PHENOLICS
ANALYSIS SHEET

Storet Number: 32730

Laboratory Code: 16

Date: _____

Sample Number: _____

Time at Start of Analysis: _____

Time at Completion of Analysis: _____

Is the Sample Spiked: Yes___ No___

Method Number: 1

Analytical Results:

Volume sample distilled _____ ml

Volume extracted _____ ml

Standard Chart:

ug phenol	Absorbance

Absorbance of sample _____

ug phenol from calibration curve _____ ug

ug/l phenol = $\frac{\text{(ug phenol)} \times 1000}{\text{ml of original sample extracted}}$ = _____ ug/l

Comments:

Analyst's Initials _____

ANALYTICAL INSTRUCTIONS

Phase II - Round Robin Study

The samples to be run in the second part of the Round Robin Study have been fixed with the EPA approved preservatives for the particular analyses indicated on the container.

You will spike only the samples for chemical oxygen demand and ammonia nitrogen as was done on the previous round of the study.

This set of samples represents a waste which should produce greater quantities of the test substances than the sample taken for Round I.

The waste should also contain greater numbers of interfering substances. The contaminants in this waste have been previously analysed over a period of time and have been found to fall within the following ranges:

Phenol	1-10 mg/l*
Ammonia-N	10-40 mg/l
Suspended Solids	30-60 mg/l
Chemical Oxygen Demand	200-500 mg/l
Oils	20-100 mg/l

* Phenols are in the milligram not microgram range.

Note: Sulfides are present in this sample in the range of 25 mg/l at the time of sampling.

The samples are to be analysed using the EPA methodology specified in Round I.

All samples will be identified as specified in the information you received for Round I. The sample information sheets will be identical to the Round I study.

Since this sample batch represents higher levels of contaminants to be found in refinery wastewaters, the spikes are accordingly higher.

By following the outlined spiking procedure, values in this specified range should be produced in addition to the background values.

Chemical Oxygen Demand	200-500 mg/l
Ammonia Nitrogen	5-10 mg/l

Procedure for Ammonia-N Spikes

To begin the analysis, open the concentrate 2 ampul by snapping the top off at the break area on the neck. Dilute 10 ml of the concentrate to 500 ml in a volumetric flask using the wastewater sample indicated for the spike. Carry out the analysis on this spiked sample in the same manner you are conducting the rest of the analytical testing for ammonia-N.

Chemical Oxygen Demand Spike

Begin the analysis by snapping off the neck of the ampul for chemical oxygen demand which has been supplied with your sample set. Dilute 15 ml of the ampul's contents to volume in a 500 ml volumetric flask using the contents of the sample indicated for COD spike. The COD analyses may now be performed in the prescribed manner.

If you have any questions, please call Billy DeFrater or Bob Benefield at the Robert S. Kerr Environmental Research Laboratory, 405/332-8800, extension 338 and 255, respectively.

You may also wish to speak to the Resident Specialist about a particular parameter. They are as follows:

Fred Pfeffer	Oil and Grease	Ext. 305
Kenneth Jackson	COD	Ext. 312
Roger Cosby	Phenols	Ext. 310
Mike Cook	Suspended Solids and Ammonia Nitrogen	Ext. 300
Clarence Edmonson	Ammonia Nitrogen	Ext. 258

APPENDIX B

SEMINAR SUMMARY

An invitation was extended to the analysts to participate in a seminar designed to furnish information on laboratory techniques for each parameter. The premise of the seminar was to minimize inherent errors in laboratory technique by reviewing stepwise procedural steps. Besides the obvious technique errors for each test procedure, analysts devised shortcuts which may magnify the obvious technique errors. The seminar was held at RSKERL with 24 in attendance. Instructors were the RSKERL analysts who participated in Phase I of the study. A tape recording was made of each lecture and a synopsis of laboratory technique problem areas by parameter follows:

CHEMICAL OXYGEN DEMAND

1. All glassware needs to be chemically clean. Steam out condensers and flasks with 50 percent sulfuric for one and one-half hours, cool, wash down condensers with distilled water and cap the condensers with aluminum foil. Wash the flasks with distilled water and cap.
2. Fix the samples with sulfuric acid.
3. Use correct volume for analysis.
4. Do not use graduated cylinders to measure the sample volume. Use large base pipettes.
5. Blend sample.
6. Use automatic pipette for potassium dichromate addition.
7. When adding sulfuric acid, keep the flask cool to the touch.
8. Wash down side of flasks.
9. Boil sample for two hours only.
10. Allow refluxed sample to cool to room temperature.
11. Results may be unreliable if it takes less than 10 ml of ferrous ammonia sulfate to titrate the dichromate to the end point.

12. Analyse reagents daily for normality.

13. Set up a blank, ferrous ammonia sulfate standard unknown and a standard, one spike per eight samples and one duplicate per eight samples for quality control.

14. Check arithmetic errors.

15. Reflux at 145° C.

16. There should not be more than 0.2 ml of potassium dichromate difference when titrating the blank and the ferrous ammonia sulfate standard.

TOTAL SUSPENDED SOLIDS

1. Thoroughly shake the sample before decanting.

2. Obtain constant weight on crucibles.

3. Always use tongs when transferring crucibles.

4. Correct oven temperature.

5. Rinse graduate with distilled water.

6. Crucibles should be chemically clean, preheated to correct temperature and cooled in a desiccant.

DISTILLATION OF AMMONIA PROCEDURE (1.0-25.0 mg/l of ammonia)

1. Ammonia free distilled water.

2. Correct normalities for reagents.

3. Fresh indicator is needed for good end point.

4. Check reagents prior to analysis for purity.

5. Boil out glass system prior to analysis.

6. Use correct aliquot of sample.

7. Check arithmetic calculations.

8. Precision and accuracy is based on sample size.

9. Titration method is better than nesserilization for industrial waste because of interfering ions.

PHENOLICS

1. Standardise stock standard by titration w/$Na_2S_2O_3$.

2. Stock standard should be refrigerated and standardised every two weeks.

3. Working phenol standard should be prepared only on the day it is used. Degradation occurs!!

4. Samples should be analysed as quickly as possible. Within four hours without preservation. Within 24 hours with preservation.

5. Always run standards for calibration curve through the phenol still the same way samples are (preservation included).

6. Guard against thermal degradation of distillate (i.e., be sure distillate is cool).

7. Buffer sample pH to 10.0 for sample prior to color development.

8. Be sure $CHCl_3$ extract is dry (free of H_2O) before reading on spectrophotometer.

OIL AND GREASE

Freon Method

This is approved method of EPA in Standard Methods for oil and grease of concentrations of <1000 mg/l.

Sample--

1. Should be collected in glass bottle (greater than 1 L) with screw cap with Teflon liner.

2. 5 ml of H_2SO_4 (1:1) should be added at time of collection.

3. pH should be <3, lower pH does not have any adverse effect.

4. When sampling any floating oil, film should be excluded.

5. Sample should be refrigerated from sample time through analysis.

6. Analysis should be started within 24 hours.

7. Glass sample bottle should have a one liter mark so as to obtain correct volume.

8. Suggestion made to use pH paper to adjust pH of sample.

Procedure--

1. Technique from Standard Methods.

2. Extract oil and grease with 40 ml of Freon; do this two times and combine, also wash sample bottle with 15-20 ml of Freon and combine with extract.

3. Distill over H_2O bath (80°-85° C).

4. Dry outside of flask, dessicate and weigh.

5. Use controlled H_2O bath, then dry air, then illuminating gas to displace the gaseous content of the flask.

6. Use tongs to handle distilling flask.

7. Obtain constant weight of flask by repeating H_2O bath, dessication, weight of flask three times.

8. Blank should be obtained by carrying 100 ml of Freon through the same procedure as the sample; it should also be dried, dessicated, and weighed three times to obtain a constant weight. The blank is then subtracted from the sample weight.

9. Volume of sample is obtained by putting sample in graduated cylinder after extraction has been done. This is more accurate than relying on marked line on sample bottle.

Advantages--

1. Freon advantages over petroleum ether or Hexane method:
   a. Freon is non-flammable,
   b. Method is faster, and
   c. Freon is heavier thus being the bottom phase in separatory funnel.

Disadvantages and Problems--

1. Prone to form emulsion with oil and grease of concentration >1000 mg/l.

2. ↑ oil and grease concentration & ↑ emulsion problem.

3. Gravimetric technique--thus have problems with analytical balance; large flask used to distill has weight of 100-120 gm.

4. Oil and grease concentration of <5 mg/l is unreliable.

5. Constant weight of 300 ml distilling flask is ± 3-4 mg/l (limitation to test).

6. Freon boiling point = 47° C--one will have problem with the concentration of contaminates in the solvent every time the container is opened and freon vapors escape.

7. Always siphon freon with glass tube, not tygon tubing, etc.

8. Emulsion problems can be improved by pH adjustment, salting, technique, or by filtration.

9. From references in Standard Methods (Taras and Blom) part of oil content is finely dispersed in sample. If sample is milky after extraction try to use Nacl to salt out oil.

10. 300 gm/l Nacl to acidified sample is mentioned in references. (5 gm/l Nacl is said to be just as effective--from EPA Lab, Edison, this can be verified by data from the RSKERL, Ada.)

11. If the salting out method is employed, use 3 to 4 aliquots of freon instead of only 2. Be sure to include this additional amount of freon in the blank calculations.

12. Or use a long-stemmed funnel with Na_2SO_4(1" layer) on glass plug. Wash with freon.

Miscellaneous--

1. Due to solvent specificity, this calculation of oil and grease should be reported as Freon extractable oil and grease content, not oil and grease.

2. Not recommended to reuse freon by condensing it.

Discussion from Group--

1. One man made mention of picking up weight which he believed came from acid. He said H_2SO_4 residue would add weight to sample. (Instructor questioned.)

2. Another man had problems with algae contamination of his samples. He tried to eliminate problem with use of gooch and glass wool, washed with freon.

5. Instructor stated work was being done on possible use of CCl_4 in some technique.

Soxhlet Method

As given in EPA Manual for oil and grease 100% mg/l:

1. Is a general physical filtration method using muslin and filter aid suspension.

2. Muslin + filter aid is extracted in soxhlet with hexane.

3. Procedure calls for 20 cycles/hr. Instructor said is was only possible to obtain 14 cycles/hr.

4. Instructor said is was possible a better method would be to add one mg filter aid to sample and shake before filtration, thus adding additional contact with filter aid.

5. Use hand covering to keep oil on hands from being added to sample. (Filter paper used to clean sample bottle and should be handled by something other than hands.)

6. If one uses plastic golves, one should run a blank to see if hexane is extracting any plastic.

7. Also, at end of procedure when drying flask, one should use dry air when solvent is being removed.